Catalytic hydrogenation of fatty acid methyl esters for gas-liquid chromatography

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[Received for publication June 15, 1961]

» In the gas-liquid chromatographic analysis of fatty acid mixtures from different natural sources, their methyl esters have generally been used. One important aid in elucidating the composition of complex fatty acid mixtures has been catalytic hydrogenation, by means of which all unsaturated fatty acids are converted into saturated acids of corresponding chain length. The catalyst often used in the laboratory is platinum oxide (1), and, according to usual instructions, the fatty acids or their methyl esters are dissolved in absolute ethanol for carrying out the procedure (1, 2, 3). We have found, however, that the use of ethanol as the solvent for the hydrogenation of methyl esters may lead to partial transethylation, with the result that the reaction product will be a mixture of methyl and ethyl esters.

Experiment 1: 1.5 g of methyl esters of fatty acids from rapeseed oil was dissolved in 40 ml ethanol, 100 mg Adams' platinum oxide catalyst (1) was added, and the mixture was hydrogenated under slightly higher than atmospheric pressure. The uptake of hydrogen was rapid during 10 to 15 minutes, then slowed down, and soon ceased entirely. The reaction mixture was left under hydrogen overnight. Then the platinum oxide was removed through filtration, and the solvent was evaporated under reduced pressure. The resulting mixture of fatty acid esters was subjected to gas-liquid chromatography in the Pye Argon Chromatograph with an ionization detector,[1] using polyethylene glycol adipate (4) at 150° as the stationary phase. The resulting chromatogram is shown in Figure 1. It is seen that there are 8 peaks in all, forming 4 pairs, of which the first member always is considerably higher than the second. By adding methyl stearate as an internal standard, it was ascertained that the peak B_1 was due to this substance. The retention volumes of the peaks A_1, C_1, and D_1 were well in accordance with the earlier determined values for the retention volumes of methyl palmitate, methyl arachidate, and methyl behenate, respectively. The peaks

[1] Manufactured by W. G. Pye & Co., Ltd., Cambridge, England.

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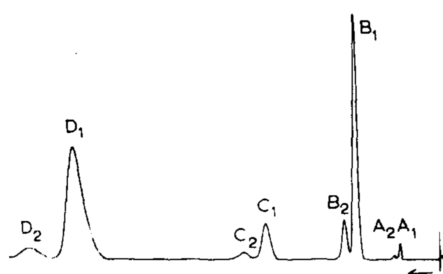

FIG. 1. Gas-liquid chromatogram of methyl esters of rapeseed oil fatty acids hydrogenated in ethanol.

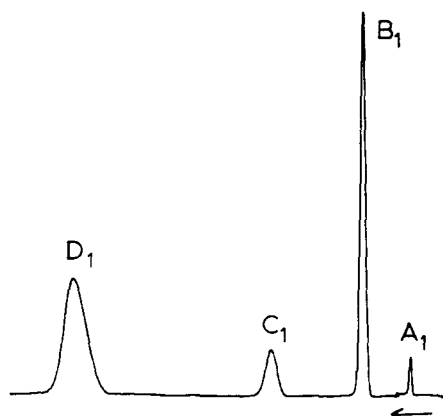

FIG. 2. Gas-liquid chromatogram of methyl esters of rapeseed oil fatty acids hydrogenated in methanol.

A_2, B_2, C_2, and D_2 were first thought to be caused by incomplete hydrogenation of the fatty acids, possibly to trans-monoenes. Some workers have called attention to the possibility of the formation of such compounds (5). This hypothesis, however, had to be abandoned, since a chromatographic run using Apiezon L at 200° as the stationary phase gave a very similar result. Had the smaller peaks been due to unsaturated fatty acid esters, they should have had smaller retention volumes and appeared earlier than the larger peaks. As their order was the same both on a polar and a non-polar stationary phase, however, they must have been due to saturated fatty acid esters. This led to the idea that during the hydrogenation in ethanol a partial transethylation might have taken place.

Experiment 2: To avoid the possibility of transethylation, another sample of the same methyl esters of fatty acids from rapeseed oil was dissolved in absolute methanol and hydrogenated by means of a procedure identical with the one described above except that the solvent was methanol instead of ethanol. The chromatogram obtained with the hydrogenated fatty acid esters on a polyethylene glycol adipate column is shown in Figure 2. It had now only 4 peaks, and their retention volumes were in complete harmony with those of methyl palmitate, methyl stearate, methyl arachidate, and methyl behenate.

Experiment 3: The ethyl esters of rapeseed oil fatty acids were prepared by boiling 50 g of rapeseed oil with 100 ml of absolute ethanol containing 5% hydrochloric acid. The esters were purified by means of a high vacuum distillation and hydrogenated in ethanol as described in Experiment 1. To the resulting hydrogenated ethyl esters, an approximately equal volume of hydrogenated methyl esters (Experiment 2) was added and the mixture was chromatographed on a polyethylene glycol adipate column. The chromatogram thus obtained showed 8 peaks whose positions were identical with the peaks observed in Experiment 1.

It is thus obvious that during the hydrogenation of fatty acid methyl esters in ethanol, a partial transethylation had taken place. To avoid this complication and the possible difficulties in interpreting the resulting chromatograms, it is advisable to use methanol instead of ethanol as the solvent in the catalytic hydrogenation of fatty acid methyl esters.

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